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JP 2000-140550

CLAIMS

[Claim(s)]

[Claim 1] A part of :aforementioned nitrous oxide [at least] which separates a nitrous oxide (N2O) from a gas flow at least and which is a process and is equipped with the following feature It is removed by at least one kind of adsorbent containing at least one kind of faujasite type zeolite. this faujasite type zeolite An Si/aluminum ratio is 1.5 or less [about 1 or more], and contains 35% or less of K+ cation, 99% or less more than per % of Na+ cation, and 99% or less more than per % of calcium2+ cation.

[Claim 2] according to claim 1 process: which has the following feature -- the above -- at least one kind of adsorbent which contains one kind of faujasite type zeolite even if few is X type zeolite or a LSX type zeolite, and an Si/aluminum ratio is 1.25 or less [about 1 or more], it is at least one kind of LSX type zeolite preferably, and the Si/aluminum ratio is the order of 1

[Claim 3] according to claim 1 or 2 process: which has the following feature -- the above -- even if few, one kind of adsorbent is the mixture of at least one kind of A type zeolite, and an at least one kind of X type zeolite or a LSX type zeolite

[Claim 4] A process given in either of the claims 1-3 which have the following feature : the aforementioned X type zeolite or a LSX type zeolite 12% or less of K+ cation is contained. And/ Or the aforementioned X type zeolite or a LSX type zeolite contains 30% or more of calcium2+ cation, preferably, contains 50% or more of calcium2+ cation, and contains 95% or less 60% or more of calcium2+ cation still more preferably.

[Claim 5] A process given in either of the claims 1-4 which have the following feature: The process concerned has further at least one step which removes "steam, a carbon dioxide, a carbon monoxide, hydrogen and a hydrocarbon, and at least one kind of impurity chosen from the groups of ethylene, propane, and/or methane" especially.

[Claim 6] The process according to claim 5 which has the following feature: Removal of some steams contained as an impurity and at least carbon dioxides is performed by at least one bed with which the activated-alumina particle was filled up.

[Claim 7] A process given in either of the claims 1-6 which have the following feature: The process concerned is a refinery process belonging to a TSA process, and is [about] preferably. -It is the TSA process performed by the temperature requirement from 40 degrees C to +80 degrees C.

[Claim 8] A process given in either of the claims 1-7 which have the following feature: In the process concerned, an adsorption step is performed by 105Pa or more pressure of 107Pa or less, and/or a desorption step is performed by 5x105Pa or less pressure of 104Pa or more, and a desorption step is preferably performed by the pressure almost equal to atmospheric pressure.

[Claim 9] given in either of claims 1-8 which have following feature process: -- further -- the above -- it has the step which reproduces one kind of adsorbent even if few, and the reproduction is preferably performed at 50-degree-C or more temperature of 250 degrees C or less

[Claim 10] A process given in either of the claims 1-9 which have the following feature: The aforementioned gas flow refined is air and is air sent to the low-temperature rectification process of air next preferably.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the process for the nitrous oxide (N_2O) contained as an impurity in the gas flow (for example, air) and a case removing a steam (H_2O), hydrocarbons (C_nH_m), and/or a carbon dioxide (CO_2) further. In case this process refines raw material air in advance of low-temperature rectification of air especially, it is effective.
[0002]
[Description of the Prior Art] About a certain kind of gas, before using it in an industrial process, it is necessary to remove beforehand the impurity contained in it.
[0003] Hydrocarbons, such as an about 250 to 500 ppm carbon dioxide (CO_2), a steam of various concentration, and/or ethylene, are usually contained in the air of the external world. Therefore, especially in advance of a low-temperature rectification process, it is necessary to remove such an impurity beforehand from air in advance of a low-temperature-separation process.
[0004] This is because it will become the factor which hydrocarbons, such as H_2O and/or ethylene, solidify [factor] under low temperature further by CO_2 and the case, and makes a heat exchanger and a fractionating tower blockade if the head end process of such air is skipped. Consequently, in one side, the capacity of equipment will be reduced and, on the other hand, the fall of the purity of the air components for recovery (oxygen or nitrogen) will be caused.
[0005] Furthermore, there is also risk of the hydrocarbon which may be contained in the air of the external world being accumulated in the liquid oxygen in a cold box, and causing explosion of a plant in that case.
[0006] in fact, low-temperature refining -- in the column, it is known that an impurity with the boiling point higher than the oxygen contained in the air of the external world will be easy to be condensed in the liquid of the pars basilaris ossis occipitalis of a fractionating tower
[0007] It is desirable to decrease the concentration of the hydrocarbon contained as an impurity in liquid oxygen as much as possible by the reasons of [clear] safe.
[0008] Generally by such reason, the preliminary refining unit of the air for removing the impurity contained in the air of the external world is prepared in the low-temperature rectification plant.
[0009] Many technology and processes are proposed for the purpose of preliminary refining of air until now.
[0010] The primary method for removing CO_2 and H_2O which are contained as an impurity in gas flows, such as air, is freezing these impurities. That is, it is solidifying or crystallizing the above-mentioned impurity in low temperature. However, from a viewpoint of equipment cost and energy cost, since it is not advantageous, this method is hardly adopted.
[0011] There is a method of adsorbing the carbon dioxide (it being a steam further by the case) contained in the gas flow of a processing object as what is replaced with this method using a suitable adsorbent. In addition, a zeolite or an activated alumina is used as this adsorbent.
[0012] The zeolite and the activated alumina belong to the adsorbent most generally used in the fact and an adsorption type gas separation process.
[0013] for this reason, the U.S. patent official report US-A -3,885,927 [No.] **** -- the example which uses X zeolite is indicated The cation exchange of this X zeolite is carried out by the barium cation 90% or more, and its surface coverage of CO_2 is high about 40% compared with X zeolite only containing a sodium cation.
[0014] furthermore, the Europe Patent Office public presentation official report EP-A -284,850 [No.] **** -- the process which refines a gas flow using a faujasite type zeolite is indicated An Si/aluminum ratio is from 1 to 2.5, and the cation exchange of this faujasite type zeolite is carried out 90% or more by the cation with bivalent strontium cation or barium cation etc.
[0015] furthermore, the U.S. patent official report US-A -4,775,396 [No.] **** -- the selective-adsorption process of the carbon dioxide contained in "sweet gas" (natural gas which does not contain the corrosive gas), such as nitrogen, hydrogen, and methane, is indicated Here, the PSA (Pressure Swing Adsorption : pressure swing adsorption) process using the fixed bed with which the faujasite type zeolite was filled up is used. The cation exchange of the faujasite type zeolite used here is carried out 20% or more by the arbitrary cations chosen from the groups which consist of zinc, rare earths, and ammonium, and a cation exchange is carried out by an alkali-metal cation or the alkaline-earth-metal cation 80% or less.
[0016] furthermore, the France public presentation official report FR-A -2,335,258 [No.] **** -- the refinery process of mixed gas is indicated This mixed gas contains nitrogen, hydrogen, an argon, and/or oxygen, and also contains a carbon monoxide, a

carbon dioxide, and water as an impurity. The above-mentioned impurity is the temperature from -40 degrees C to +4 degrees C, and is adsorbed by A type zeolite or X type zeolite. The cation exchange of the A type zeolite indicated by this reference is carried out by the calcium cation 80% or less 72% or more, and the Si/aluminum ratio is a maximum of 1. Moreover, a cation exchange is not carried out and the Si/aluminum ratio is [the thing to which the cation exchange of the X type zeolite was carried out, or] 1.5 or less [1.15 or more]. In addition, as for 1.15 or less X type zeolite, the Si/aluminum ratio is called as usual the LSX zeolite (low silica X zeolite) or silica reduction zeolite.
[0017] the same -- the Europe Patent Office public presentation official report EP-A -0,718,024 [No.] **** -- the process which removes CO2 out of a gas flow is indicated using X type zeolite The Si/aluminum ratio of this X type zeolite is the maximum abbreviation 1.15. Adsorption temperature is [about]. -It is the range of 50 to +80 degrees C. The result at the time of using X type zeolite or a LSX zeolite is also further indicated by this reference. The cation exchange of these X type zeolites or the LSX zeolite is not carried out, or a cation exchange is carried out by a lithium, calcium, or the rare earth cation.
[0018] furthermore, the former Soviet Union patent official report SU-A -1,357,053 [No.] **** -- mordenite type zeolite ("mordenite-type zeolite") ******** -- it is indicated In order that this mordenite type zeolite may remove a nitrous oxide, a cation exchange is carried out by the barium cation, and the reproduction temperature of this adsorbent is about 180 degrees C.
[0019] furthermore, the old East Germany patent official report DD-A -657,053 [No.] **** -- the method of using an adsorbent for preservation of food and purifying environment is indicated This adsorbent is mixture which consists of activity carbon and an A type zeolite in which the cation exchange was carried out by the calcium cation.
[0020] However, it is not thought that the conventional process mentioned above should be satisfied completely.
[0021] The reason is used in order to remove CO2 and the steam with which some adsorbents, such as standard 13X zeolite, are usually contained in air, about some of other compounds which may be contained in air, for example, ethylene, a propane, methane, ethane, and/or a nitrous oxide, is caught partially or is not caught at all.
[0022] This is "Linde Reports on Science and Technology, 36/1983, Dr J.Reyhing". It is indicated by inner report: "removal of the hydrocarbon from the process of an air separation plant using the molecular-sieve adsorbent." Similarly, this is "MUST'96" "Munich Meeting on AirSeparation Technology, Octover 10-11, 1996, Dr U.Wenning"). It is indicated by inner report: "the nitrogen oxide in an air separation plant." It is emphasized there that 5A type zeolite is not effective in prehension of the nitrous oxide contained in air.
[0023] As mentioned above, when the ethane contained by various concentration as an impurity in air, a propane, a nitrous oxide, and ethylene are taken into consideration, generally the following can be said.
[0024] (a) To liquid oxygen, ethylene is the unsaturated hydrocarbon of fusibility, has a low solute-gas equilibrium constant, and is dissolved to the level of 30,000 ppm. Therefore the temperature of the liquid oxygen in 1.2x105Pa is -181 degrees C, the congealing point of ethylene is -169 degrees C, on the other hand preliminary processing of air is not performed, or preliminary processing is inadequate, and when ethylene is not caught completely, ethylene exists by the solid state in a low-temperature plant.
[0025] (b) Ethane and a propane exist in the state of a liquid at the aforementioned temperature of the liquid oxygen in 1.2x105Pa.
[0026] (c) A nitrous oxide (N2O) causes another problem in the supercold separation unit of air. The nitrous oxide is anywhere contained on the level of 0.3 ppm in the atmosphere, and is increasing to 0.3% of order every year. Unlike the hydrocarbons mentioned previously, into liquid oxygen, a nitrous oxide is inactive and causes no risk in the state. However, almost always, a nitrous oxide enters into the fractionating tower of a supercold separation unit, and forms a solid sediment in a heat exchanger and a fractionating tower like a carbon dioxide. Since such a sediment becomes the factor which reduces the performance of equipment, it is desirable to prevent the deposition.
[0027] however, usable on the industrial scale for now removing the nitrous oxide (NO2) contained as an impurity in the gas flow (especially -- the inside of air) -- the effective process is not known actually
[0028] in addition, the Europe Patent Office public presentation official report EP-A -862,938 [No.] **** -- in order to remove NOx(es), especially N2O, it recommends using the zeolite adsorbent (especially 13X type zeolite) with which the cation exchange is not performed however, it mentions later -- as -- this invention -- according to the result of the comparison test carried out by persons, especially 13X type zeolite is not effective in fact, in order to catch N2O
[0029] Furthermore, the way purging or low-temperature adsorption removes these impurities is also learned so that these impurities may not reach saturation level in a supercold separation unit.
[0030] However, the latter method is [0031] which is not completely considered to be satisfied from a viewpoint on cost (especially energy cost) very disadvantageously therefore.
[Problem(s) to be Solved by the Invention] Therefore, by improving the conventional refinery process, the purpose of this invention be to improve the reliability of an industrial plant, and, specifically, be in the thing which be include as an impurity in a gas flow (inside of the raw material air especially send to a low-temperature rectification process) and which solve the problem about the removal method of a nitrous oxide (N2O) (they be ethylene or other hydrocarbons further according to the case) especially.
[0032]
[Means for Solving the Problem] A part of :aforementioned nitrous oxide [at least] which this invention is a process which separates a nitrous oxide (N2O) from a gas flow at least, and is equipped with the following feature It is removed by at least one kind of adsorbent containing at least one kind of faujasite type zeolite. this faujasite type zeolite An Si/aluminum ratio is 1.5 or

less [about 1 or more], and contains 35% or less of K+ cation, 99% or less more than per % of Na+ cation, and 99% or less more than per % of calcium2+ cation.
[0033] The process of this invention is equipped with the feature beyond following 1 or it according to a situation.
[0034] (a) the above -- at least one kind of adsorbent which contains one kind of faujasite type zeolite even if few is X type zeolite or a LSX type zeolite, and an Si/aluminum ratio is 1.25 or less [about 1 or more], it is at least one kind of LSX type zeolite preferably, and the Si/aluminum ratio is the order of 1
[0035] (b) the above -- even if few, one kind of adsorbent is the mixture of at least one kind of A type zeolite, and an at least one kind of X type zeolite or a LSX type zeolite
[0036] (c) The aforementioned X type zeolite or a LSX type zeolite contains 25% or less of K+ cation, and contains 12% or less of K+ cation preferably.
[0037] (d) The aforementioned X type zeolite or a LSX type zeolite contains 30% or more of calcium2+ cation, preferably, contains 50% or more of calcium2+ cation, and contains 95% or less 60% or more of calcium2+ cation still more preferably.
[0038] (e) The aforementioned process has further at least one step which removes "steam, a carbon dioxide, a carbon monoxide, hydrogen and a hydrocarbon, and at least one kind of impurity chosen from the groups of ethylene, propane, and/or methane" especially.
[0039] (f) Removal of some steams contained as an impurity and at least carbon dioxides is performed by at least one bed with which the activated-alumina particle was filled up.
[0040] (g) The aforementioned process is a refinery process belonging to a TSA (Temperature Swing Adsorption; temperature swing adsorption) process, and is [about] preferably. -It is the TSA process performed by the temperature requirement from 40 degrees C to +80 degrees C.
[0041] (h) In the aforementioned process, a desorption (discharge) step is performed by 5x105Pa or less pressure of 104Pa or more, preferably, is performed by 1.4x105Pa or less pressure of 0.9x105Pa or more, and is performed by the pressure almost equal to atmospheric pressure still more preferably.
[0042] (i) In the aforementioned process, an adsorption step is performed by 105Pa or more pressure of 107Pa or less, and is preferably performed by 3x105Pa or more adsorptive pressure force 6x106Pa or more.
[0043] (j) the aforementioned process -- further -- the above -- it has the step which reproduces one kind of adsorbent even if few, and perform the reproduction preferably at 50-degree-C or more temperature of 250 degrees C or less
[0044] (k) In the aforementioned process, the aforementioned gas flow refined is air and is air sent to the low-temperature rectification process of air next preferably.
[0045] The term called "air" into this application specification means the air of the circumference taken in in the outdoor atmosphere or the building, and the heated enclosure that encloses or is not heated. In addition, as for this "air", preliminary processing may be performed beforehand. There is change (for example, especially an addition or removal of oxygen or nitrogen) of oxidization and dehumidification partial at least using the oxidation catalyst as this preliminary processing, or composition of the composition gas etc.
[0046] Moreover, further, cation ** of the cations of alkaline earth metal especially magnesium, strontium, and/or barium is contained in X type zeolite or a LSX type zeolite, and there may also be things in it.
[0047] Moreover, an adsorption step is performed using at least one adsorption unit. Preferably, an adsorption step is performed using two adsorption units prepared in parallel. In the case of the latter, reproduction of the adsorption unit of another side is performed on stream [one adsorption unit].
[0048] Moreover, the refinery process of the aforementioned gas flow contains at least one step for reproducing an adsorbent further. At this step, with 0-degree-C or more temperature of 300 degrees C or less, preferably, it is 250 degrees C or less in 50-degree-C or more temperature, and the flash plate of the adsorbent is carried out using remaining nitrogen or other remaining gas for reproduction.
[0049]
[Embodiments of the Invention] Next, the example of the refinery process of the gas flow based on this invention is explained in detail using a drawing. However, these examples do not limit the technical range of this invention at all.
[0050] (Example 1)
It had "composition of LSX (Si/aluminum=1) type zeolite" faujasite structure, and the Si/aluminum ratio performed composition of 1.15 or less X type zeolite (the so-called LSX type zeolite) based on the conventional method. In addition, this synthetic method is for example, the British patent official report. GB-A -1,580,928 [No.] It is indicated.
[0051] Generally in X type zeolite obtained as a result, 30% or less of potassium cation and 90% or less of 60% or more sodium cation contained 20% or more 40% or less 10% or more. In addition, this does not deny the possibility of the existence of other cations.
[0052] The LSX type zeolite containing both potassium and sodium is usually called NaKLSX.
[0053] Thus, the cation exchange was given to compounded NaKLSX and the cation (especially calcium) of other metals beyond a kind or it was incorporated. The calcium cation replaced a part of potassium cation [at least] which it can come and is therefore contained in Above NaKLSX, and/or a part of sodium cation [at least] to the target rate level of exchange.
[0054] If it puts in another way, NaKLSX to CaNaKLSX (hereafter referred to as "CaLSX") will be obtained. That is, NaKLSX containing a calcium cation is obtained in part all of potassium cations, or by replacing all or a part of sodium cation by the calcium cation.

[0055] In fact, preferably, the PSA (Pressure Swing Adsorption; pressure swing adsorption) type process which targets especially removal of N2O contained in the gas flow (especially inside of air), or when a zeolite is used in a TSA (Temperature Swing Adsorption; temperature swing adsorption) type process, especially the calcium cation contained in the LSX type zeolite has big influence on the adsorptivity ability of a zeolite to N2O, so that it may mention later.

[0056] (Example 2)

15 ppm C2H4** contacted the nitrogen added artificially to the particle of 10X zeolite by "adsorption of C2H4 or CO2 by CaX zeolite" 400ppm CO2 (curve C10), or the case. This 10X zeolite (it is hereafter called a "CaX zeolite") is replaced by the calcium cation to about 96%, and the 4 remaining% is K+ cation and Na+ cation substantially.

[0057] CO2 by the CaX zeolite or adsorption of C2H4 was performed by pressure:6x105Pa, temperature:20 degree C, and flow rate:8.8Sm3/h. The laboratory type adsorption unit with a diameter of 60mm was filled up with the CaX zeolite.

[0058] The CaX zeolite particle had about 2mm mean particle diameter, and the thickness of a zeolite floor was 250mm.

[0059] The breakthrough curve (breakthrough time) obtained about CO2 and C2H4 by drawing 1 is shown. the CaX zeolite based on this invention removed the carbon dioxide effectively for about 70 minutes (curve C11), and has removed ethylene effectively for about 300 minutes so that drawing 1 may show (curve C12) -- in addition in this application specification, "breakthrough time" means time until CO2 (C2H4) of 1 ppm level is detected by the downstream of a bed from the start of adsorption

[0060] (Example 3)

"comparison test: -- adsorption [of C2H4 and CO2 by 13X zeolite with which the cation exchange is not performed]" -- Example 3 is the result of evaluating CO2 or the adsorptivity ability to C2H4 like Example 2 using the conventional 13X zeolite particle to which the cation exchange is not performed

[0061] The test using this 13X zeolite was performed on the same conditions as the test using the CaX zeolite shown in Example 2. However, in this test, after adding artificially 450 ppm CO2 (curve C20) or C2H4 [14 ppm] (curve C22) to nitrogen, this was contacted to the above-mentioned 13X zeolite.

[0062] The result obtained by drawing 2 is shown. When 13X zeolite with which the cation exchange is not given is used so that drawing 2 may show, the breakthrough of CO2 happens after about 90 minutes (curve C21). This time is slightly long compared with the case where a CaX zeolite is used.

[0063] In addition, the curve C20 and the curve C22 are shown in drawing 2 for comparison. These curves express impurity composition of a CO2 in the upstream of a bed and the content of C2H2, i.e., the gas flow before refining, respectively.

[0064] When 13X zeolite with which the cation exchange is not given is used contrary to the result which receives CO2, the breakthrough of C2H4 happens after about 30 minutes (curve C23). On the other hand, the breakthrough at the time of using the CaX zeolite based on this invention has happened after 300 minutes, as shown in Example 2.

[0065] As for the CaX zeolite based on this invention, the above result shows that the adsorptivity ability to ethylene is improved notably compared with the conventional 13X zeolite with which the cation exchange is not performed.

[0066] (Example 4)

"N2O using the CaX zeolite (calcium is contained 60%), and adsorption of CO2" -- the test shown in this example 4 was performed by the same method as the test shown in previous Example 2 The purpose of this test is to evaluate the breakthrough time to the nitrous oxide (N2O) of a CaX zeolite adsorbent based on this invention.

[0067] In order to perform this, after adding a 0.9 ppm nitrous oxide (N2O) artificially to nitrogen, this was contacted to the bed with which the particle of a CaX zeolite was filled up like the case of Example 2. In addition, this CaX zeolite (it is hereafter called a "CaX zeolite") is replaced by the calcium cation to about 60%.

[0068] The particle size of a CaX zeolite particle was about 2mm.

[0069] Other experiment conditions are the same as that of the case of Example 2.

[0070] The result obtained by drawing 3 is shown. The breakthrough of N2O happens after about 60 minutes so that drawing 3 may show (curve C31). Having the performance by which the zeolite based on this invention adsorbs N2O effectively by this was checked.

[0071] In addition, the curve C30 and the curve C32 are shown in drawing 3 for comparison. As for the curve C30, the curve C32 expresses the breakthrough curve of CO2 for the content (400 ppm) of CO2 in the upstream of a bed, respectively.

[0072] This result shows that the breakthrough of CO2 happens almost simultaneously with the breakthrough of N2O, when CaX is used.

[0073] (Example 5)

X type zeolite with which substitution by the calcium cation was performed was saturated by the 0.5 ppm nitrous oxide (N2O) in pressure:6x105Pa to "reproduction of CaX zeolite saturated with N2O" 60%.

[0074] Subsequently, at the temperature (curve C40) of a maximum of 260 degrees C, the above-mentioned zeolite was contacted with the flow of the gas for reproduction (for example, nitrogen), and was reproduced.

[0075] The flows of the gas for reproduction were collected at the outlet of an adsorption unit, and were analyzed, and change of the amount (curve C41) of N2O from which it was desorbed (discharge) was measured. In addition, this change is dependent on the temperature of elapsed time and the gas for reproduction.

[0076] The result is shown in drawing 4 . Almost all N2O by which the CaX zeolite was adsorbed has ****ed at the temperature of 100 degrees C or less so that drawing 4 may show (discharge).

[0077] As mentioned above, although the CaX zeolite has strong compatibility to N2O rather than 13X zeolite, it turns out in the

case of reproduction of a zeolite that desorption of N2O by which the CaX zeolite particle was adsorbed can be performed on the same conditions as what was performed from the former to 13X zeolite particle. That is, it can be made to reproduce by carrying out the flash plate of the adsorbent particle by hot (specifically before or after 100 degrees C) gas.

[0078] If it puts in another way, according to this invention, reproduction of the CaX zeolite particle used for adsorption of N2O contained in the gas flow as an impurity can be carried out as compared with the conventional process (adsorption process of especially a TSA type) which uses 13X zeolite, without making energy cost increase.

[0079] (Example 6)

"N2O using the CaX zeolite (calcium is contained 86%), and adsorption of CO2" -- the test of this example 6 was performed by the same method as the test of previous Example 4 The purpose of this test is to evaluate the breakthrough time to the nitrous oxide (N2O) of an adsorbent based on this invention. The CaX zeolite used in this example is replaced by the calcium cation to 86%. In addition, the CaX zeolite used in Example 4 is replaced by the calcium cation to 60%.

[0080] After adding a 0.9 ppm nitrous oxide (N2O) artificially to nitrogen, or after adding artificially about 445 ppm carbon dioxide (CO2) (curve C50), this was contacted to the particle of the CaX zeolite replaced by the calcium cation to 86%.

[0081] In addition, other experiment conditions are the same as that of the case of Example 4.

[0082] The result obtained by drawing 5 is shown. drawing 5 shows -- as -- the breakthrough (curve C52) of N2O, and the breakthrough of CO2 -- (a curve C51) -- it both happens after about 60 minutes The result in Example 4 (drawing 3) was reconfirmed by this. That is, having the performance by which the zeolite based on this invention adsorbs N2O and CO2 effectively was checked.

[0083] (Example 7)

"comparison test: -- N2O by 13X zeolite with which the cation exchange is not performed, and adsorption [of CO2]" -- the same test as Example 4 and Example 6 was performed using the conventional 13X zeolite adsorbent with which the cation exchange is not performed

[0084] this after adding about 5.5 ppm N2O and about 374 ppm CO2 with the flow of raw material nitrogen in this test -- pressure:6x105Pa and temperature: -- the particle of 13X zeolite was made to contact at about 20.5 degrees C

[0085] The result is shown in drawing 6 . Unlike the CaX zeolite based on this invention, the conventional 13X zeolite with which the cation exchange is not performed cannot catch N2O so that drawing 6 may show.

[0086] When the conventional 13X zeolite is used as an adsorbent in a TSA process, this is understood from what the breakthrough of N2O happens after 15 or 20 minutes (curve C60), and the breakthrough of CO2 happens after about 60 minutes (curve C61), as shown in drawing 6 .

[0087] (Example 8)

The air of the external world containing C2H4 and 400 ppm CO2 ("refining of air using CaX (Si/aluminum=1.25)" 0.4ppm N2O and 1 ppm) was contacted to X type zeolite (Si/aluminum=1.25). In addition, this X type zeolite is replaced by the calcium2+ cation to 60%, and contains about 27% of Na+ cation, and about 13% of K+ cation.

[0088] Adsorption temperature was about 20 degrees C, and the adsorptive pressure force was about 6x105Pa.

[0089] Air was collected and analyzed after refining. Consequently, to the air refined by making it this appearance, it became clear that N20, C2H4, and CO2 are not contained substantially.

[0090] 13X zeolite replaced by the calcium2+ cation to 60% is the capacity of a far small adsorbent compared with the conventional 13X zeolite which is not replaced, and can catch simultaneously N20, C2H4, and CO2 in air.

[0091] (Example 9)

"refining of the air using CaLSX (Si/aluminum=1)" -- the test of this example 6 was performed by the same method as the test of previous Example 4 That is, the air of the external world containing 0.4 ppm C2H4 and 400 ppm CO2 (N2O and 1 ppm) was contacted to the LSX type zeolite (Si/aluminum**1). In addition, this LSX type zeolite (low silica type zeolite) is replaced by the calcium2+ cation to about 85%, and, otherwise, contains Na+ cation and K+ cation (Na++K+<=15%).

[0092] Adsorption temperature was about 20 degrees C, and the adsorptive pressure force was about 6x105Pa.

[0093] Air was collected and analyzed after refining. Consequently, to the air refined by making it this appearance, it became clear that N20, C2H4, and CO2 are not contained substantially.

[0094] It was checked that the LSX zeolite replaced by the calcium2+ cation to 85% can catch simultaneously N20, C2H4, and CO2 in air.

[Translation done.]